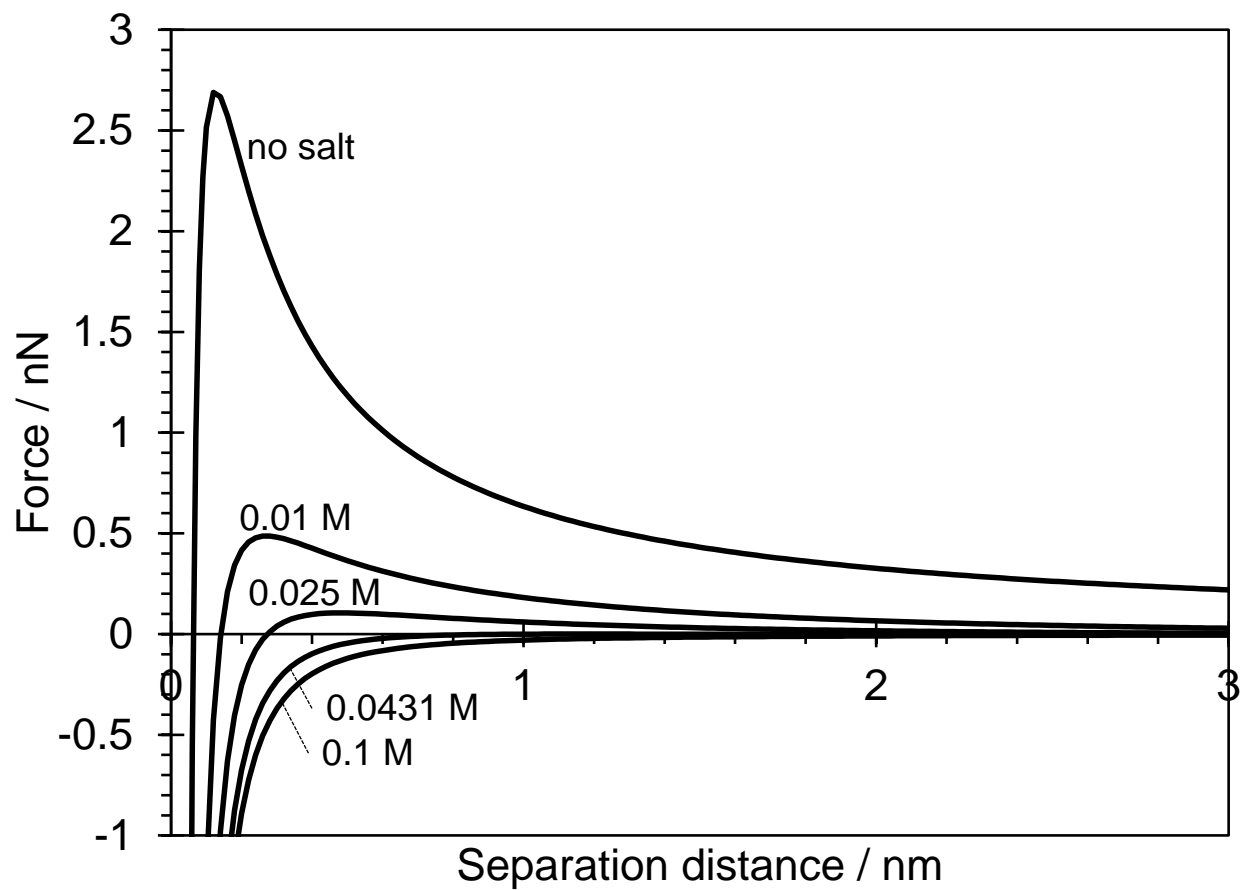


## Supporting Information

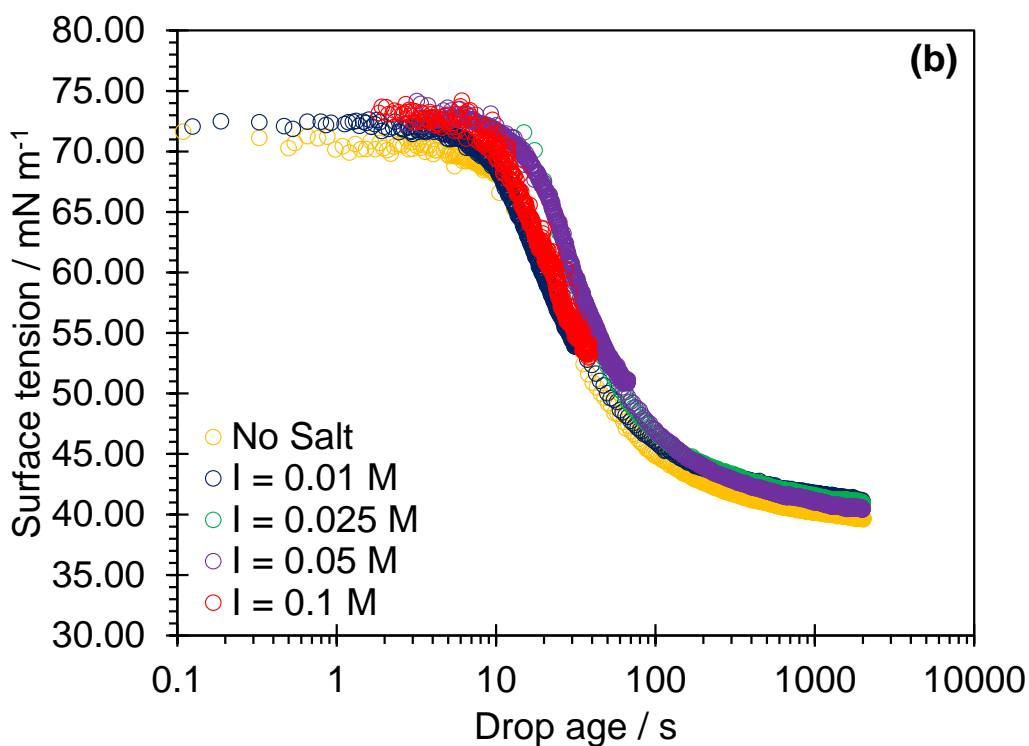
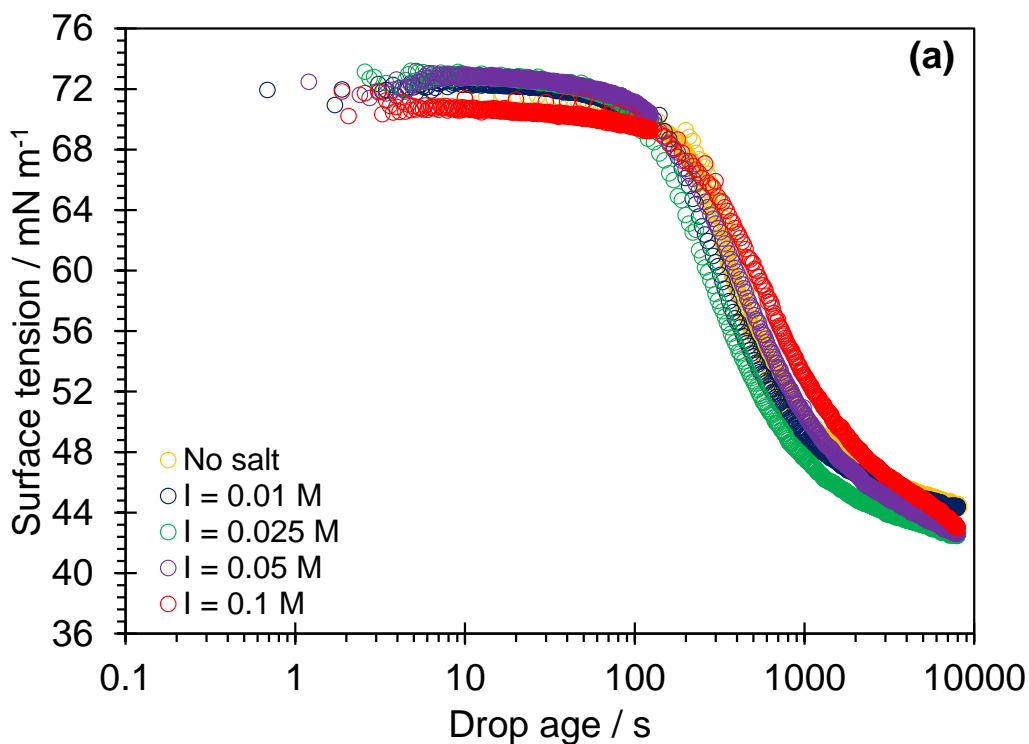
### **Effects of Ionic Strength on the Colloidal Stability and Interfacial Assembly of Hydrophobic Ethyl Cellulose Nanoparticles**

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**Figure S1.** Total interaction force between two EC nanoparticles of the same size (radius  $44 \pm 5$  nm) which is computed from extended-DLVO theory<sup>1</sup> at various ionic strengths. At ionic strength of 0.0431 M the coagulation criteria (i.e.,  $F=0$  and  $dF/dh=0$ ) are satisfied.



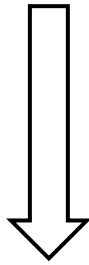
**Figure S2.** Dynamic surface tension (DST) measurements of colloidal solutions of EC nanoparticles at constant concentration of EC nanoparticle (a)  $0.2 \text{ g L}^{-1}$  and (b)  $0.8 \text{ g L}^{-1}$ .

**Table S1.** Measurements of zeta potential as a function of ionic strength.

<b>Ionic strength (M)</b>	<b>Average Zeta potential (mV)</b>	<b>Standard deviation</b>	<b>Number of measurements</b>
0	-59.08	1.67	6
0.01	-40.37	2.11	23
0.025	-30.49	2.52	13
0.05	-18.10	0.91	12
0.07	-16.13	1.51	17
0.1	-15.00	1.11	23

**Table S2.** Statistical analysis of contact angles measured at different levels of ionic strength. It is assumed that each set of measurements has the same variance and the conclusions are based on 95% confidence interpretation.

Ionic strength (M)	Contact angle (degrees)	Standard deviation	Number of measurements
0	71.09	0.52	5
0.025	71.47	0.77	5
0.1	71.47	0.39	5



**Hypothesis test:**

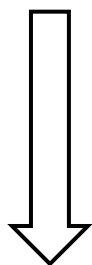
**Null hypothesis:** No difference between the mean values

**Alternative hypothesis:** There is a difference between the mean values.

Comparison pair	$t_{obs.}$	$T_{critical}$ (from t-distribution table)	Conclusion
0 M vs. 0.025 M	0.91	2.31	$t_{obs.} < T_{critical} \rightarrow$ Fail to reject the null hypothesis $\rightarrow$ No difference between the contact angles at different levels of ionic strength is detected.
0.025 M vs. 0.1 M	0	2.31	
0 M vs. 0.1 M	1.30	2.31	

**Table S3.** Factorial statistical analysis of EC nanoparticle radius (after ~ 2h) at different levels of ionic strength and EC nanoparticle concentration. It is assumed that each set of measurements has the same variance and the conclusions are based on 95% confidence interpretation.

EC concentration (g L <sup>-1</sup> )	Ionic strength (M)	Average particle radius (nm)	Standard deviation	Number of measurements
0.2	0.01	42.09	4.62	3
	0.025	48.18	1.31	3
	0.05	69.84	2.26	3
	0.1	923.4	159.5	3
0.5	0.01	44.28	6.86	3
	0.025	47.58	0.56	3
	0.05	67.78	12.06	3
	0.1	780.8	108.8	3
0.8	0.01	33.90	3.56	3
	0.025	44.81	5.68	4
	0.05	536.1	120.6	3
	0.1	804.8	40.22	3



**Hypothesis test:**

**Null hypothesis:** No difference between the mean values

**Alternative hypothesis:** There is a difference between the mean values.

Comparison pair		t <sub>obs.</sub>	T <sub>critical</sub> (from t-distribution table)	Conclusion
EC 0.2 g L <sup>-1</sup>	0.01 M vs. 0.025 M	2.19	2.78	1
	0.01 M vs. 0.05 M	9.33	2.78	2
	0.025 M vs. 0.05 M	14.34	2.78	
EC 0.5 g L <sup>-1</sup>	0.01 M vs. 0.025 M	0.83	2.78	1
	0.01 M vs. 0.05 M	2.93	2.78	2
	0.025 M vs. 0.05 M	2.90	2.78	
EC 0.8 g L <sup>-1</sup>	0.01 M vs. 0.025 M	3.11	2.57	2
	0.01 M vs. 0.05 M	7.21	2.78	
	0.025 M vs. 0.05 M	7.05	2.57	

1.  $t_{\text{obs.}} < T_{\text{critical}}$  → Fail to reject the null hypothesis → There is no significant difference between the nanoparticle size.
2.  $t_{\text{obs.}} > T_{\text{critical}}$  → Reject the null hypothesis → There is a significant difference between the nanoparticle size.

Note that there is an obvious difference between the EC nanoparticle radius at ionic strength of 0.1 M and other levels of salt concentration. Therefore, the statistical hypothesis test is conducted only for ionic strengths equal to or smaller than 0.05 M.

The highlighted comparison which shows a statistically significant difference between the average nanoparticle size at  $I = 0.01\text{M}$  and  $I = 0.025\text{M}$  is considered to be the result of an outlier DLS measurement (33.9 nm).

**Table S4.** ANOVA table of computed adsorption energy ( $|\Delta E|$ ) at different ionic strength. The analysis is conducted at 95% confidence level for a 3x5 factorial design.

<b>Source</b>	<b>Sum of square</b>	<b>Degree of freedom</b>	<b>Mean square</b>	<b>s.e.</b>	<b><math>t_{df(=30), 0.025}</math></b>	<b>LSD</b>
EC concentration	1.09E+9	2	5.47E+8			
Ionic strength	5.01E+8	4	1.25E+8			
Interaction	1.15E+9	8	1.44E+8			
Treatment	2.74E+9	14	-			
Error	1.44E+9	30	4.78E+7	6.92E+3	2.04	1.41E+4
Total	4.18E+9	44	9.50E+7			



**Table S5.** Statistics (mean and standard deviation) of the late-time DST slope ( $(dy/dt^{-1/2})|_{t \rightarrow \infty}$ ) reported in Table 1.

EC concentration (g L <sup>-1</sup> )	Ionic strength (M)	Slope (N m <sup>-1</sup> s <sup>0.5</sup> )	Standard deviation	Label
<b>0.2</b>	0	0.2620	0.020494	<b>1</b>
	0.01	0.2459	0.027313	<b>2</b>
	0.025	0.2382	0.051476	<b>3</b>
	0.05	0.3544	0.191579	<b>4</b>
	0.1	0.4568	0.067102	<b>5</b>
<b>0.2</b>	0	0.093	0.01	<b>I</b>
	0.01	0.0971	0.012046	<b>II</b>
	0.025	0.0883	0.015646	<b>III</b>
	0.05	0.125	0.067268	<b>IV</b>
	0.1	0.1424	0.017218	<b>V</b>
<b>0.8</b>	0	0.0604	0.002718	<b>i</b>
	0.01	0.0560	0.008466	<b>ii</b>
	0.025	0.0647	0.008562	<b>iii</b>
	0.05	0.0699	0.000636	<b>iv</b>
	0.1	–		

**Hypothesis test:**

**Null hypothesis:** No difference between the mean values

**Alternative hypothesis:** There is a difference between the mean values.

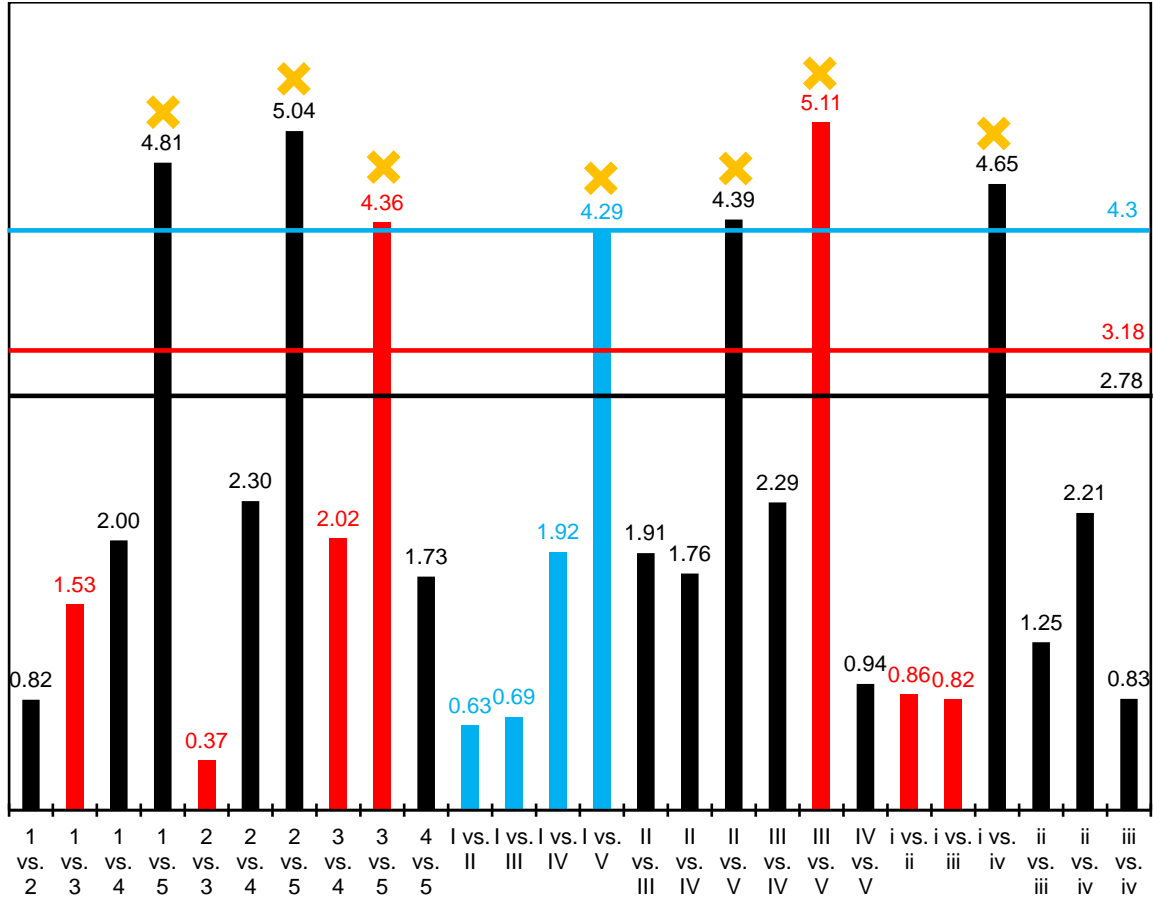
1.  $t_{obs.} < T_{critical}$  → Fail to reject the null hypothesis → There is no significant difference between the slopes.
2.  $t_{obs.} > T_{critical}$  → Reject the null hypothesis (marked by a **x**) → There is a significant difference between the slopes.

All possible comparisons are shown in the following figure.  $t_{obs}$  is calculated from

$$\frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

number of replicates, respectively and subscripts 1 and 2 show two different series.  $T_{critical}$  is found from  $t$ -table at a 95% confidence level. The black, red, and blue bars

should be compared to the  $T_{critical}$  indicated by the black, red, and blue lines, respectively.



## **Bulk nanoparticle concentration is not significantly reduced by coagulation during the early stages of adsorption**

Two dynamic processes are competing in suspensions of EC nanoparticles of ionic strength at or beyond CCC: coagulation in the bulk and adsorption-driven interfacial assembly. It is shown<sup>1</sup> that the initial coagulation rate is

$$\dot{R}_{coag}\Big|_{t \rightarrow 0} = -k_{coag} C_0^2 V \quad (S1)$$

where  $k_{coag}$  is the coagulation rate constant (here estimated using eq 2),  $C_0$  is the particle concentration, and  $V$  is the bulk volume. The initial rate of adsorption at early time is expressed as follows<sup>2</sup>

$$\dot{R}_{ads}\Big|_{t \rightarrow 0} = -k_a C_0 S \quad (S2)$$

where  $k_a$  is the adsorption rate constant and  $S$  is the area of the interface. For the pendant drop experiments,  $V$  is the volume ( $\sim 10 \mu\text{L}$ ) and  $S$  is the surface area of the drop, respectively. Assuming spherical drops one obtains

$$\frac{\dot{R}_{coag}\Big|_{t \rightarrow 0}}{\dot{R}_{ads}\Big|_{t \rightarrow 0}} = \frac{k_{coag} C_0 R}{3k_a} \quad (S3)$$

where  $R$  is the radius of the pendant droplet. Considering the values reported in this study ( $k_{coag} \sim O(10^{-17}) \frac{m^3}{s}$ ,  $k_a \sim O(10^{-6}) \frac{m}{s}$ ,  $C_0 \sim O(10^{-17}) \frac{particle}{m^3}$ ,  $R \sim O(10^{-3}) m$ ), one

obtains  $\frac{\dot{R}_{coag}\Big|_{t \rightarrow 0}}{\dot{R}_{ads}\Big|_{t \rightarrow 0}} \sim O(10^3)$  for EC nanoparticle suspensions above the CCC. Although

the rate of coagulation is initially  $\sim 1000$  times faster than the rate of adsorption, the bulk concentration changes only by  $\sim 0.001\%$  during the early stages (first 60 s) of the process. This supports the assumption that the bulk concentration remains constant during the early stages of adsorption regardless of EC concentration and ionic strength.

## REFERENCES

- (1) Holthoff, H.; Schmitt, A.; Fernández-Barbero, A.; Borkovec, M.; Cabrerizo-Vílchez, M. Á.; Schurtenberger, P.; Hidalgo-Álvarez, R. Measurement of absolute coagulation rate constants for colloidal particles: Comparison of single and multiparticle light scattering techniques. *J. Colloid Interf. Sci.* **1997**, *192*, 463-470.
- (2) Bizmark, N.; Ioannidis, M. A.; Henneke, D. E. Irreversible adsorption-driven assembly of nanoparticles at fluid interfaces revealed by a dynamic surface tension probe. *Langmuir* **2014**, *30* (3), 710-717.